In situ infrared transmission study of Rb- and K-doped fullerenes

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We have measured the four IR-active C_{60} molecular vibrations in $M_x C_{60}$ (M =K, Rb) as a function of doping x. We observe discontinuous changes in the vibrational spectra showing four distinct phases (presumably $x = 0, 3, 4$, and 6). The 1427-cm^{-1} and 576-cm^{-1} modes show the largest changes shifting downward in frequency in four steps as the doping increases. Several very weak modes are visible in the $x = 6$ phase and are possibly Raman modes becoming weakly optically active. We present quantitative fits of the data and calculate the electron-phonon coupling of the 1427 cm^{-1} IR mode.

The discovery of superconductivity in alkali-metal-doped C_{60} (Ref. 1) has prompted a great deal of excitement and a large body of research. Since electron-phonon coupling proved to be responsible for superconductivity in many materials, the relation between the charge carriers and the lattice vibrations is important. Here we present a study of the infrared-active molecular vibrations of $M_x C_{60}$ as a function of alkali-metal doping x for (M = K and Rb). We show the shift of some IR modes to lower frequencies in discrete steps, corresponding to the four known stable phases, $x = 0, 3, 4, 6$. We also perform an analysis of how the change in the vibrational modes is related to the introduction of carriers into the lowest unoccupied molecular orbital band of C_{60}.

The truncated icosahedral structure of C_{60} fullerenes belongs to the icosahedral point group I_h and has four infrared-active intramolecular vibrational modes with F_{1u} symmetry.[2] These modes, with center frequencies $\nu_1 = 527, \nu_2 = 576, \nu_3 = 1182$, and $\nu_4 = 1427$ cm^{-1}, have been experimentally observed.[3,4] The 527- and 576-cm^{-1} modes are associated with primarily radial motion of the carbon atoms, while the 1182- and 1427-cm^{-1} modes are primarily tangential motion.[2]

In the $M_x C_{60}$ compounds, the alkali atoms give up one electron each to the lowest unoccupied molecular orbital (LUMO) of a C_{60} molecule. As long as the on-site Coulomb repulsion is not too large the triply degenerate t_{1u} LUMO can hold six electrons.[5] Therefore the t_{1u} orbital is half filled by three electrons, the material is metallic, and it superconducts at low temperatures.[1] Completely filling the t_{1u} orbital with six electrons makes the C_{60} a band insulator and the structure becomes body-centered cubic.[6] An insulating phase at $x = 4$ has also been observed with a body-centered-tetragonal structure.[7]

The C_{60} for this study was prepared using the well-known technique of Kratschmer *et al.*[4] The resultant fullerene powder was loaded into a tantalum boat and heated to about 500 °C in a vacuum of $\sim 1 \times 10^{-6}$ Torr to vapor deposit C_{60} inside the sample cell. Film thickness was monitored by counting visible light interference fringes as the C_{60} was deposited. Typical sample thickness was about 1.2 μm.

Our miniature sample cells are constructed of glass with two silicon windows, one of which serves as a substrate for the C_{60}. A small appendage contains the alkali metal, and the entire sample chamber is sealed under high vacuum. The transmission spectra were obtained as the sample was doped with a Bomem MB-155 Fourier-transform infrared (FTIR) spectrometer at 2 cm^{-1} resolution covering a 400–6000 cm^{-1} frequency range. Four-probe resistivity of the film was measured simultaneously. By carefully warming the alkali metal to increase the vapor pressure and by heating the C_{60} film to increase the diffusion rate of the metal into the film, a slow, continuous doping was achieved. During potassium doping, the substrate was maintained at 120 °C and the metal at 100 °C. For Rb, the corresponding temperatures were 85 °C and 70 °C, respectively. The infrared spectra were obtained with the film samples at their substrate temperatures.

The results of the infrared spectroscopy *in situ* with alkali-metal doping are displayed in Figs. 1 and 2. Since at low frequencies the transmitted intensity is roughly proportional to the square of the resistivity, the IR measurement by itself is a good indicator of the doping process. Indeed, both the dc resistivity and the transmission exhibit a minimum as the doping proceeds. Kochanski *et al.* associate this minimum with the metallic $M_3 C_{60}$ phase.[8] Upon further doping, the resistivity reaches a maximum, corresponding to the insulating $M_6 C_{60}$ phase, after which the resistivity drops, but the features in the spectra change little, indicating that the sample begins to coat with alkali metal and the C_{60} is fully doped ($x = 6$). At this stage, closer visual inspection reveals metallic films on the window surfaces.

We have performed quantitative fits to both sets of doping data. The vibrational spectra are accurately fit using a dielectric function composed of Lorentzian oscillators and a dc conductivity to mimic the changing conductivity observed as doping progresses. This yields the center frequency ω_0, strength S, and width Γ of each mode. We present the results and our assignments of corresponding phases in Table I. We interpret the data as follows: As the doping proceeds, layers of $M_3 C_{60}$ grow followed by similar layers of $M_4 C_{60}$ and $M_6 C_{60}$. We ob-
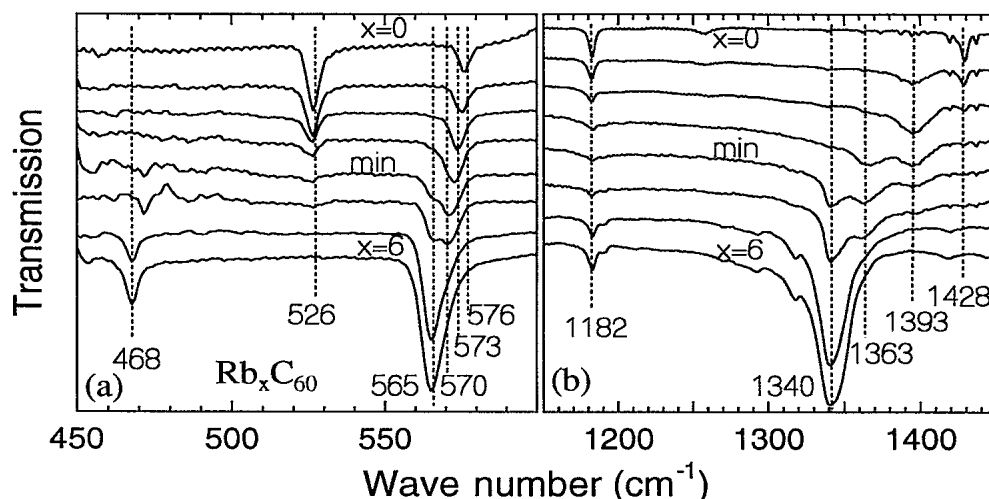
<u>47</u>   14 607

FIG. 1. Rb_xC_{60} infrared transmission spectra as a function of x. (a) shows the lower two vibrational modes (ν_1 and ν_2) and (b) shows the upper two modes (ν_3 and ν_4). The curves are offset for clarity. Undoped C_{60} is the top curve and the sample is further doped going down in the figure. The bottom curve is for fully doped Rb_6C_{60}. The minimum in the resistivity of the sample corresponds to the curve labeled "min." Vertical lines are guides to indicate the assignments of vibration frequencies, as obtained from numerical fits.

serve that the ν_1 mode at 526 cm^{-1} gets weaker as the sample loses all $x = 0$ phase and reappears at 468 cm^{-1} in the $x = 6$ phase. The ν_2 mode shifts in discrete steps and grows in strength during the doping process. This effect is most clearly visible for the Rb doping where it shifts from 576 to 573 to 570 to 565 cm^{-1}. Using the x-ray results,[9,10,7,6] which indicate that only the $x = 0$, 3, 4, and 6 phases are stable at this temperature, we associate these modes with the $x = 0$, 3, 4, and 6 phases, respectively. The ν_3 mode at 1182 cm^{-1} is enhanced by a factor of almost 2 in the $x = 6$ phase. Looking at the ν_4 mode, we can again see distinct phases. This mode is enhanced by a factor of 80 in the $x = 6$ phase.

The shifts in the ν_2 and ν_4 modes for the K-doped sample show only three clear phases. This may be due to more uniform doping of the K_xC_{60} sample, as it is known that K diffuses more rapidly into C_{60} than Rb.[11] Vibrational modes are more difficult to detect in a homogeneous metallic film since the high reflectivity, due

to conduction electrons, dominates the response.

The resultant values for the $x = 6$ data in this work are in excellent agreement with previous IR measurements on M_6C_{60} published by Fu et al.[12] The phase separation seen in our data is also in agreement with previous Raman-spectroscopy results[11,13] where, for example, the change in the $A_g(2)$ pinch mode originally at 1458 cm^{-1} clearly shows distinct phase separation. Note that this mode, like the ν_4 mode in the IR spectrum, involves stretching of the C=C double bonds.

The Rb_6C_{60} and K_6C_{60} spectra also show some very weak modes at 1461, 1418, 1317, 1284, 1240, 1190, 1146, 943, 688, 645, and 532 cm^{-1}. These are similar in frequency to several Raman-active modes for C_{60} (1458, 1430, 1396, 1315, 1241, 1190, 1140, 950, and 533 cm^{-1}) and Rb_6C_{60} (1477, 1431, 1322, 1235, 1121, 1091, 689, and 655 cm^{-1}).[11,14,15] We may be observing Raman modes becoming weakly IR active in our fully doped samples. Some of these modes are not allowed by the symmetry
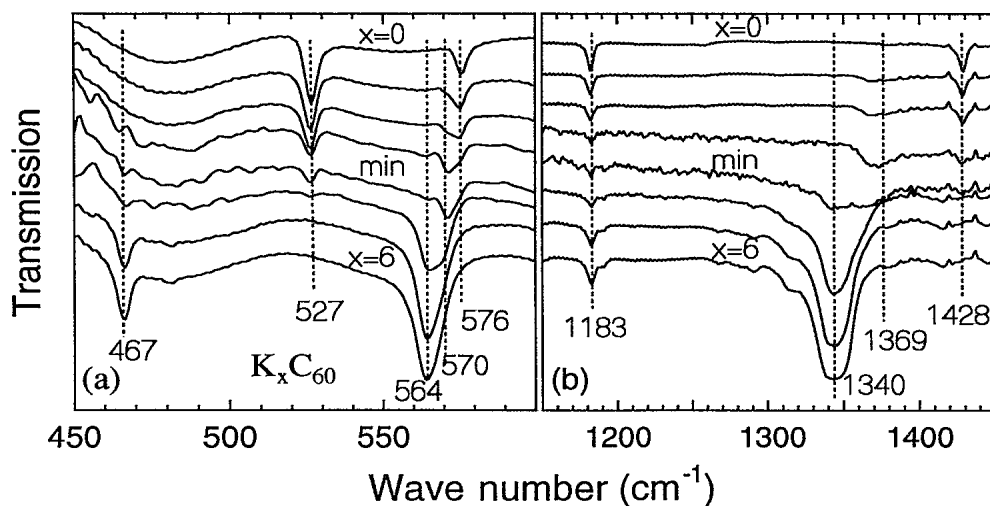

FIG. 2. Same as Fig. 1 now for K_xC_{60}.

TABLE I. Lorentzian oscillator fits to the four IR intramolecular vibrations of $M_x C_{60}$ (M =Rb and K) assigned to the different stable phases ($x = 0, 3, 4, 6$). The numbers are essentially the same for both dopants except as noted. ω_0 is the center frequency, S is the strength ($S = \omega_p^2/\omega_0^2$), and Γ is the width of each vibrational mode.

		C_{60}	M_3C_{60}	M_4C_{60}	M_6C_{60}
	ω_0 (cm^{-1})	526		472	467
ν_1	S	0.02		0.008	0.03
	Γ (cm^{-1})	2.5		1.5	3
	ω_0 (cm^{-1})	576	573	570	565
ν_2	S	0.008	0.019	0.022	0.17
	Γ (cm^{-1})	2.7	3	3.7	2.8
	ω_0 (cm^{-1})	1182			1182
ν_3	S	0.0018			0.003
	Γ (cm^{-1})	4.2			5.8
	ω_0 (cm^{-1})	1428	1393	1363[a]	1340
ν_4	S	0.001	0.012	0.016	0.08
	Γ (cm^{-1})	4.5	20.8	23	7.2

[a]Values in table are for Rb$_4$C$_{60}$. K_4C_{60} differs for ν_4 : $\omega_0 = 1369$ cm^{-1}, $S = 0.028$, and $\Gamma = 21$ cm^{-1}.

of the single molecule, but they have been observed in Raman spectra of crystalline C_{60}.[14,15] It should be noted that the changes in the vibrational modes due to photoexcitation of carriers[16] are different from the changes reported here for chemical doping.

The charged-phonon theory by Rice and Choi[17] predicts many of the features we observe, in particular, the enhancement of the strength and the softening of the 1428 cm^{-1} mode upon doping. In Fig. 3 we illustrate how the addition of electrons to a complex molecule can enhance the strength of a "silent" IR-active phonon. Figure 3(a) depicts an eigenmode of the molecule, characterized by two pairs of atoms oscillating in opposite phase. This mode is "IR active" in the sense that it has odd symmetry. However, as long as only symmetric electronic states are allowed, the mode is "silent" since there is no net dipole moment in the direction of the electric field. In Fig. 3(b) we allow for asymmetric states, i.e., electron transfer between the two pairs of atoms. The electron transfer naturally couples to the atomic displacements via the rearrangement of electronic states, and it also generates an electric dipole moment. Rice and Choi[17] argue that in C_{60}, electrons excited between the t_{1u} and the next-higher-energy t_{1g} molecular orbitals create a coupling to the infrared-active vibrational modes, and simultaneously soften the vibration frequency (Fig. 4). In view of the agreement between the experiment and theory for the ν_4 mode, it is all the more surprising that the ν_1 mode does not follow the same behavior. We argue that this mostly radial mode is more sensitive to the intermolecular forces, and its frequency is influenced by the fcc-to-bcc phase transition.
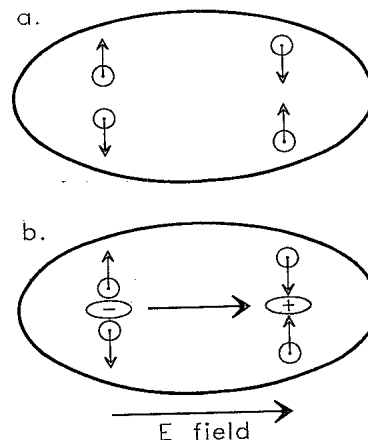

FIG. 3. Schematic illustration of charge-transfer induced infrared activity. The arrowed circles represent atoms moving withing a single "molecule"; the symmetry of the oscillation is odd. In (a) only even electronic states are allowed and therefore the strength of the IR-active vibration is small. In (b) the electron transfer couples the mode to the external field by introducing a dipole moment.

As long as the electron is confined to a single molecule, symmetry arguments predict that the intraband electron-phonon scattering, relevant to superconductivity, is dominated by Raman modes. Therefore, the attempts to explain superconductivity in the fullerenes focused on the Raman-active A_g and H_g modes.[18] However, for extended electronic or vibrational states, the IR modes may become important too. In fact, we see evidence for damping of the vibrational modes by conduction electrons. According to the sum rule, $\sum_i \Gamma_i/\omega_{0i}^2 = (\pi/2)N(E_F)\lambda$,[19] the broadening of the vibrational mode is related to the electron-phonon coupling. The largest change, 16.3 cm^{-1}, in the widths was observed in the ν_4 mode. This leads to a contribution of 0.055 states/eV in $N(E_F)\lambda$ for each of the three degenerate modes. Considering that there are 180 vibrational modes for the C_{60} molecule,
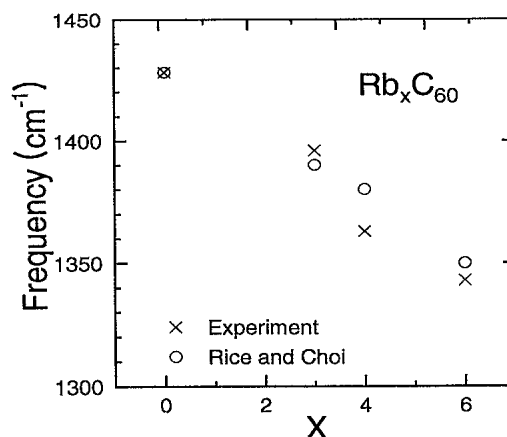

FIG. 4. Frequency of the ν_4 IR mode vs the inferred composition for Rb-doped C_{60}. Circles refer to the calculation of Rice and Choi (Ref. 15).

a coupling of this magnitude is significant although the strongest electron-phonon coupling seen to date is for the $H_g(2)$ Raman mode (0.25 states/eV).[15] It remains to be seen how important this coupling is for superconductivity.

In summary, we have measured the four infrared-active intramolecular vibrational modes of C_{60} as a function of Rb and K doping. Quantitative presentation of our measurements and assignments of the modes to different stable phases of $M_x C_{60}$ were made. We show that our results are consistent with previous work and describe how the data could relate to a superconducting pairing mechanism in these materials.

[1] A.F. Hebard et al., Nature **350**, 600 (1991); K. Holczer et al., Science **252**, 1154 (1991); M. J. Rosseinsky et al., Phys. Rev. Lett. **66**, 2830 (1991).

[2] R. E. Stanton and M. D. Newton, J. Phys. Chem. **92**, 2141 (1988); Z. C. Wu et al., Chem. Phys. Lett. **137**, 291 (1987).

[3] W. Kratschmer, K. Fostiropoulos, and D. R. Huffman, Chem. Phys. Lett. **170**, 167 (1990); W. Kratschmer et al., in Dusty Objects in the Universe, edited by E. Bussoletti and A. A. Cittone (Kluwer, Dordrecht, 1991); S. Bethune et al., Chem. Phys. Lett. **179**, 181 (1991).

[4] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature **347**, 354 (1990).

[5] R.C. Haddon, Acc. Chem. Res. **25**, 127 (1992).

[6] O. Zhou et al., Nature **351**, 462 (1991).

[7] R. M. Fleming et al., Nature **352**, 701 (1992); Peter W. Stephens et al., Phys. Rev B **45**, 543 (1992).

[8] G. P. Kochanski, A. F. Hebard, R. C. Haddon, and A. T. Fiory, Science **255**, 184 (1992).

[9] R. M. Fleming et al., in Clusters and Cluster-Assembled Materials, edited by R. S. Averback, D. L. Nelson, and J. Bernholc, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 691.

[10] P. W. Stephens et al., Nature **351**, 632 (1991).

[11] S. J. Duclos, R. C. Haddon, S. Glarum, A. F. Hebard, and K. B. Lyons, Science **254**, 1625 (1991).

[12] K.-J. Fu et al., Phys. Rev. B **46**, 1937 (1992).

[13] T. Pichler, M. Matus, J. Kurti, and H. Kuzmany, Phys. Rev. B **45**, 13841 (1992).

[14] P.H.M. van Loosdrecht, P.J.M. van Bentum, and G. Meijer, Phys. Rev. Lett. **68**, 1176 (1992).

[15] Michael G. Mitch, Sabrina J. Chase, and Jeffrey S. Lannin, Phys. Rev. Lett. **68**, 883 (1992).

[16] G. Lawrence Carr, Michael C. Martin, D. Koller, and L. Mihaly (unpublished); Y. H. Kim, F. Li, and F. Diederich, Phys. Rev. B **45**, 10169 (1992).

[17] M. J. Rice and H.-Y. Choi, Phys. Rev. B **45**, 10173 (1992).

[18] R. A. Jishi and M.S. Dresselhaus, Phys. Rev. B **45**, 2597 (1992); M. Schluter et al., Phys. Rev. Lett. **68**, 526 (1991); C. M. Varma, J. Aanen, and K. Raghavachari, Science **254**, 989 (1991); F. C. Zhang, M. Ogata, and T. M. Rice, Phys. Rev. Lett. **67**, 3452 (1991).

[19] P. B. Allen, in Dynamical Properties of Solids, edited by G. K. Horton and A. A. Maradudin (North-Holland, New York, 1980), Vol. 3, p. 95.

Erratum: *In situ* infrared transmission study of Rb- and K-doped fullerenes [Phys. Rev. B 47, 14607 (1993)]

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The preliminary assignments in this paper of the positions of the $x = 3$ and $x = 4$ IR lines were incorrect. Further unambiguous x-ray identification of the $x = 1$ phase[1] indicates that the correct assignments of the $F_{1u}(4)$ vibration are 1428 cm^{-1} for C_{60}, 1393 cm^{-1} for M_1C_{60}, 1363 cm^{-1} for $M_{3,4}C_{60}$, and 1340 cm^{-1} for M_6C_{60} in agreement with recent work by Kuzmany *et al.*[2] The middle two column titles of Table I and the middle two experimental points in Fig. 4 should be adjusted accordingly.

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[1]Michael C. Martin, Daniel Koller, Xiaoqun Du, Peter W. Stephens, and Laszlo Mihaly, Phys. Rev. B **49**, 10818 (1994).

[2]T. Pichler and H. Kuzmany, in *Electronic Properties of Fullerenes and Other Novel Materials*, Proceedings of the International Winterschool, Kirchberg, Tyrol, 1993, edited by H. Kuzmany *et al.* (Springer-Verlag, Berlin, 1993); T. Pichler, R. Winkler, and H. Kuzmany (unpublished).